Chapter 3 — Final Methomyl Exposure Characterization

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1 Environmental Transport and Fate Characterization

Physical-chemical properties and dissipation-related parameters for methomyl are provided in <u>Table 3-1</u>. Data summarized here include data submitted to the U.S. EPA and open literature data including ECOTOX studies classified as ECOTOX plus. Open literature data were included when the information was determined to add to the overall understanding of the environmental fate of methomyl.

Methomyl enters the environment via direct spray and spray drift onto soil, foliage, and/or water. The environmental fate properties of methomyl along with monitoring data identifying its presence in surface waters indicate that important transport pathways include runoff and spray drift. Volatilization, atmospheric transport, and subsequent deposition of methomyl to aquatic and terrestrial habitats may occur. Wu *et. al.* (2014) estimated the atmospheric life-time of 224 days for Z-methomyl and 160 days for E-methomyl at 25°C based on average OH radical concentration of 9.7 x 10^5 cm⁻³ in atmosphere. However, its vapor pressure (5.4 x 10^{-6} torr) and Henry's Law Constant (2.1 x 10^{-11} atm-m³/mol) indicate that it has a low potential to volatilize and long-rage transport is most likely not a major pathway of concern.

Based on methomyl's aerobic soil metabolism and aerobic and anaerobic aquatic metabolism data, methomyl is not considered persistent¹ in the environment, with half-lives on the order of days to weeks (representative² half-life values range from 2.5 to 52 days). Under anaerobic conditions methomyl degradation is likely to be faster than under aerobic conditions (Smelt *et al.*, 1983), particularly in the presence of reduced iron (Bromilow *et al.*, 1986). It is stable to hydrolysis at lower pHs (neutral to acidic), but it degrades slowly in alkaline conditions (DT₅₀ = 36-266 days). Hydrolysis half-lives indicate that methomyl is classified as persistent in aquatic and terrestrial environments where microbial activity is not present; however, microbial activity is expected in most natural environments.

Degradation kinetics calculations were checked in 2019 to be consistent with the most recent guidance (USEPA, 2015). However, between the release of the Draft BE in early 2020 and this Final BE, the hydrolysis half-life for methomyl was increased from 266 days (used in this assessment) to 522 days, based on hydrolysis data that was reviewed for the 2020 drinking water assessment (DWA) that was completed for methomyl (USEPA, 2020). A sensitivity analysis was performed to assess the resultant change from increasing the half-life from 266 days to 522 days as well as increasing the half-life from 266 days to stable on the current risk picture for ESA species. The resultant EECs showed that the aquatic modeling performed for methomyl is not sensitive to changes to the hydrolysis half-life and both the increase to 522 days and the increase to stability resulted in less than a 1% change in EECs. Therefore, the EECs were not recalculated to reflect the change in the hydrolysis rate from 266 to 522 days for the Final BE.

¹ Based on the Toxic Release Inventory classification system where half-lives greater than 60 days in water, soil, and sediment are considered persistent and half-life greater than 6 months are considered very persistent (USEPA, 2012a).

² Half-live values were recalculated using the North American Free Trade Agreement (NAFTA) guidance in estimating degradation kinetics (NAFTA, 2012; USEPA, 2012b).

Linear sorption coefficients were checked and utilized in this assessment to be consistent with current modeling input guidance (USEPA, 2009). Methomyl is classified as mobile $(K_{FOC}s)$ range from 32-61 L/kg)³ and has the potential to reach surface water through runoff and soil erosion. Overall, soil/sediment-water distribution coefficients increase with increasing percent of organic-carbon. Methomyl has the potential to reach groundwater especially in high-permeability soils with low organic-carbon content and/or the presence of shallow groundwater. The maximum depth of leaching in the terrestrial field dissipation studies is 30 inches. Predominantly methomyl will be present in the water column and to a lesser extent as bound to sediments. Based on measured octanol-water partition coefficients $(K_{ow}s)$ and $K_{FOC}s$, exposure to sediment-dwelling organisms is likely to occur in lesser extent as compare to organisms in water column. Low octanol/water partition coefficient also suggests that the chemical will have a low tendency to accumulate in aquatic and terrestrial organisms.

Terrestrial field dissipation half-lives from the surface soil of cropped cabbage fields ranged from 4-6 days in Mississippi to 54 days in California. Two factors may explain the differences in dissipation between the two sites. Soil moisture content, which may affect the level of biological activity, varied between the two sites (moisture contents ranged from 2.5% to 17% in the California soils and averaged 16% over the first 15 days in the Mississippi soils). The Mississippi site received more rainfall, which may have led to more leaching out of the surface. In both studies most of the methomyl residues were found in the upper 30 cm of soil.

A small-scale prospective ground-water monitoring study was conducted for methomyl. Lannate L, a formulated product of methomyl, was applied to a site cropped in sweet corn in Cook County, Georgia. Methomyl was not detected in ground water except detections occurred in 12-foot depth suction lysimeters at concentrations up to $0.943~\mu g/L$.

Air monitoring data collected from the 1960s through the 1980s, and summarized by Majewski and Capel (1995), do not indicate the presence of methomyl in the atmosphere, due in large part to the lack of testing for methomyl. The authors' reviewed a single study which tested for methomyl in ambient air at three residential sites near an agricultural area in Salinas, California which were sampled during a high pesticide use month. Methomyl was not detected at any of the air monitoring sites (the level of detection was 35 nanograms per cubic meter).

Table 3-1. Physical/Chemical and Environmental Fate Properties of Methomyl.

Chemical Fate/Parameter	Range of Values (Number of Values)				
Common name	Methomyl	Sources			
Structure	N O N N	https://pubchem.ncbi.nlm.nih.gov/co mpound/5353758			

³ Mobility was classified using the Food and Agriculture Organization (FAO) classification system (FAO, 2000) and supplemental sorption coefficients.

Chemical Fate/Parameter		Range of Values (Numb	er of Values)
Common name		Methomyl	Sources
IUPAC Name		-methyl (<i>EZ</i>)- <i>N-</i> amoyloxy)thioacetimidate	
Chemical Formula		C ₅ H ₁₀ N ₂ O ₂ S	MRID 48597001
Molecular Mass (g/mole)		162.2 g/mol	
Vapor Pressure (Torr, 25°C)		5.4×10 ⁻⁶	MRID 41209701
Henry's law constant	i .	10 ⁻¹¹ (atm-m³/mol) 56E-10 (unitless)	Estimated from MRID 41209701, and MRID 41402101
Solubility (20°C) (mg/L)		5.5x10 ⁴	MRID 41402101
Octanol-water partition coefficient (log K _{ow})		0.12	MRID 00157991
Hydrolysis half-life @ 25°C (days)	pH 5 no evidence of degradation pH 7 no evidence of degradation pH 9 36		MRID 00131249
	pH 7	266	Chapman and Cole, 1982
	pH 7	522	MRID 48217705
Aqueous photolysis half-life @ 25°C (days)	Stable at pH 7 (buffer), 50 days (Natural water) 42 days (pH 7 buffer w/ 100 M excess nitrate) 8.5 days (pH 7 buffer w/ 1000 M excess nitrate)		MRID 43823305 (supplemental)
Soil photolysis half-life (days)	34 (silt l	oam, pH 6.8, 24-28°C)	MRID 00163745 (acceptable)
Aerobic soil metabolism half-life (days)	52 (silt 11.6 (5.3 (sand 8.3 (l 7.3 (sand	MRID 00008568 (acceptable) MRID 43217901 (acceptable) MRID 45473401 (acceptable)	
Anaerobic soil metabolism half- life (days)	7 (flowing cor 14 (stati	Not Persistent ^A Indition, Ioam, pH 7.8, 25°C) Ic, Ioam, pH 7.8, 25°C) Not Persistent ^A	MRID 43217902 (acceptable)
Aerobic aquatic metabolism half-life (days)	3.5 (cla 4.8 (silty o	y loam, pH 6.8, 20°C) clay loam, pH 7.6, 20°C) Not Persistent ^A	MRID 43325401 (supplemental)

Chemical Fate/Parameter	Range of Values (Number of Values)				
Common name	Methomyl	Sources			
Anaerobic aquatic metabolism half-life (days)	2.5 (loam, pH 5.9, 20±2 °C) 20.5 (loamy sand, pH 8.0, 20±2 °C)	MRID 49245302 (supplemental)			
Organic-carbon normalized soil -water distribution coefficients (Koc) L/kgoc	36 (silt loam) 39 (sandy loam) 45 (silt loam) 65 (sandy loam) Mobile ^B	MRID 00161884 (acceptable)			
Terrestrial field dissipation DT ₅₀ s	5 – 54	MRIDs 41623901, 41623902, 42288001, 43217903			
Bioconcentration factor (L/kg)	No data				

A Based on the Toxic Release Inventory classification system where half-lives greater than 60 days in water, soil, and sediment are considered persistent and half-life greater than six months are considered very persistent (USEPA, 2012a).

2 Identification of Transformation Products of Concern

Major methomyl degradates include methomyl oxime (S-methyl-N-hydroxythioacetimidate), acetonitrile, acetamide, and CO_2 . Methomyl oxime (S-methyl-N-hydroxythioacetimidate) was detected at a maximum of 44% in the alkaline hydrolysis study. Acetonitrile was detected at a maximum of 66%, 40% and 27% in the aqueous photolysis, soil photolysis and aerobic aquatic metabolism studies, respectively. Acetamide was detected at 14% in the aerobic aquatic metabolism study. CO_2 was detected at 22.5-75% in the aerobic soil, anaerobic soil, and aquatic metabolism studies. The only non-volatile degradate in the laboratory studies was methomyl oxime (S-methyl-N-hydroxythioacetimidate). It was present at high concentrations in the alkaline hydrolysis study but was only a minor degradate in the aerobic soil metabolism, anaerobic soil metabolism, photolysis and aerobic aquatic metabolism studies. There are data demonstrating the formation of methomyl sulfoxide during disinfection (chlorination) in water treatment (MRID 46210701), although this compound was not found in any environmental fate studies.

None of the major methomyl degradates identified in the environmental fate studies is considered to be of toxicological concern based on the available data. None of these degradates contain a carbamate functional group. Furthermore, based on previous a Quantitative Structural-activity Relationship (QSAR) analyses, the degradates are estimated to be less toxic than the parent (see **USEPA**, **2012c**. Therefore, the potential risks associated with the degradates will not be quantitatively assessed because risks associated with the degradates are not expected to materially influence (*i.e.*, change) any species-specific effects determination that is based on methomyl parent.

^B Mobility was classified using the Food and Agriculture Organization (FAO) classification system (FAO, 2000).

3 Measures of Aquatic Exposure

In general, maximum application rates and minimum application retreatment intervals are modeled to estimate the exposure to methomyl based on the master use summary document (APPENDIX 1-2) developed for methomyl, unless otherwise noted.

Methomyl-specific modeling scenarios are used for modeling each use. This includes the selection of scenarios and agronomic practices (*e.g.*, applications methods, dates). <u>Table 3-4Table 3-4</u> include model input parameters as well as the justification for selecting these parameters; however, the general approaches used are described below.

3.1 Aquatic Exposure Models

Aquatic exposures (surface water and benthic sediment pore water) are quantitatively estimated for representative methomyl uses included on the master use summary document (APPENDIX 1-2) by HUC 2 Regions (Figure 3-1 Figure 3-1) and by aquatic bin (2-7) using the Pesticide Root Zone Model (PRZM5) and the Variable Volume Water Model (VVWM)⁴ in the Pesticides in Water Calculator (PWC). As mentioned elsewhere, the flowing aquatic bins include bin 2 low flow, bin 3 moderate flow, and bin 4 high flow. The static aquatic bins include bin 5 low volume, bin 6 moderate volume, and bin 7 high volume. Additional information on aquatic bins is available in ATTACHMENT 1-2.

Aquatic bin 1 represents aquatic habitats associated with terrestrial habitats (e.g., riparian zones, seasonal wetlands) and is simulated using the PRZM5/VVWM and the Plant Assessment Tool (Section 3.5). Aquatic bins 8 and 9 are intertidal and subtidal near shore habitats, respectively, and aquatic bin 10 is the offshore marine habitat. EFED does not currently have standard conceptual models designed to estimate EECs for these estuarine/marine systems. EFED and the Services have assigned surrogate freshwater flowing or static systems to evaluate exposure for these estuary and marine bins. Aquatic bin 5 will be used as surrogate for pesticide exposure to species in tidal pools; aquatic bins 2 and 3 will be used for exposure to species at low and high tide, and aquatic bins 4 and 7 will be used to assess exposure to marine species that occasionally inhabit offshore areas.

EFED modeled these flowing and static bins in previous Biological Evaluations (BEs) by using watershed drainage areas developed from flowing waterbody relationships and static bin runoff estimates (USEPA, 2016a; USEPA, 2016b; USEPA, 2016c). However, the results have not been as expected. In short, one would expect daily concentrations in flowing bins to be lower than those in static bins, given that water, and any pesticide, is flowing out of the system. However, in most of the modeling runs the EECs for the flowing bins were higher, and in many cases an order of magnitude higher, than the static bins. In large part, the higher EECs were the result of modeling a large watershed using assumptions that were designed to simulate a smaller watershed. For example, it was assumed that the watershed was entirely treated on the same day. For a large watershed, it was not expected that this assumption was appropriate. For the static waterbodies, the watershed-to-waterbody ratio was not really known but

⁴ The exposure models can be found at: https://www.epa.gov/pesticide-science-and-assessing-pesticide-risks/models-pesticide-risk-assessment

was derived by determining the watershed size needed to generate runoff sufficient to fill the waterbody. This relationship relied on modeling conducted using topography, surface soil characteristics, and precipitation specific to the PWC model and scenarios considered highly vulnerable to surface water runoff. As a result, there was much uncertainty with the EECs that were being generated from the modeling in the previously completed BEs.

For methomyl, when using PWC, EFED has relied on two standard waterbodies which have been traditionally used in EFED to estimate EECs for the various bins. The standard farm pond was used to develop EECs for the medium and large static bins (e.g., bins 6 and 7) and the index reservoir for the medium and large flowing bins (e.g., bins 3 and 4). For the smallest flowing and static bins (bin 2 and 5), EFED derived edge of field estimates from the PRZM daily runoff file (e.g., ZTS file). Error! Reference source not found. Table 3-2 provides a crosswalk of the bins and how they were modeled.

While the standard farm pond is bigger than bin 6, the EECs estimated for bin 6 in previous BEs were similar to those generated for bin 7, and so an economy of modeling was deemed appropriate.

While the index reservoir has a much lower effluent flowrate than bins 3 and 4, it has been used as a vetted flow-through waterbody for EFED for years, with an accepted watershed-to-waterbody ratio developed for an actual vulnerable watershed (Shipman Reservoir, Shipman, IL) and has been reviewed by a previous Federal Insecticide Fungicide Rodenticide Act (FIFRA) Scientific Advisory Panel (SAP) (Jones and Abel, 1997; USEPA, 1998)). EFED expects the EECs that are generated using the index reservoir to be a conservative surrogate for those observed in bins 3 and 4. The watershed area associated with the index reservoir is roughly an order of magnitude smaller than the average area for a HUC 12 (the smallest areal delineation for an aquatic species range), but within the range of minimum and maximum values $(9.54 \times 10^7 \, \text{m}^2, 2.08 \times 10^3 - 9.24 \times 10^9 \, \text{m}^2)$.

Lastly, bins 2 and 5 are very small waterbodies and the EECs in them would be reflective of concentrations in a headwater stream or a standing puddle that received runoff at the edge of a treated field. As such, edge-of-field concentrations were estimated and used as a surrogate for EECs in these waterbodies.

Table 3-2. Aquatic Bin, Modeled Waterbody Crosswalk.

Aquatic Bin	Description	Width (m)	Length (m)	Depth (m)	Flow (m³/s)	Waterbody Used for Modeling
1	Wetland	64	157	0.15	Variable ¹	Custom
2	Low-flowing waterbody	2	Field ²	0.1	0.001	Edge-of-field
3	Medium-flowing waterbody	8	Field ²	1	1	Index reservoir
4	High-flowing waterbody	40	Field ²	2	100	Index reservoir
5	Low-volume, static waterbody	1	1	0.1	N/A	Edge-of-field
6	Medium-volume, static waterbody	10	10	1	N/A	Farm pond
7	High-volume, static waterbody	100	100	2	N/A	Farm pond

More detailed information can be found in **ATTACHMENT 3-1. Background Document Aquatic Exposure Estimation for Endangered Species**.

 $^{^{\}mathrm{1}}$ The depth and flowrate in this waterbody is variable, depending on rainfall.

 $^{^2}$ The habitat being evaluated is the reach or segment that abuts or is immediately adjacent to the treated field. This habitat is assumed to run the entire length of the treated area.

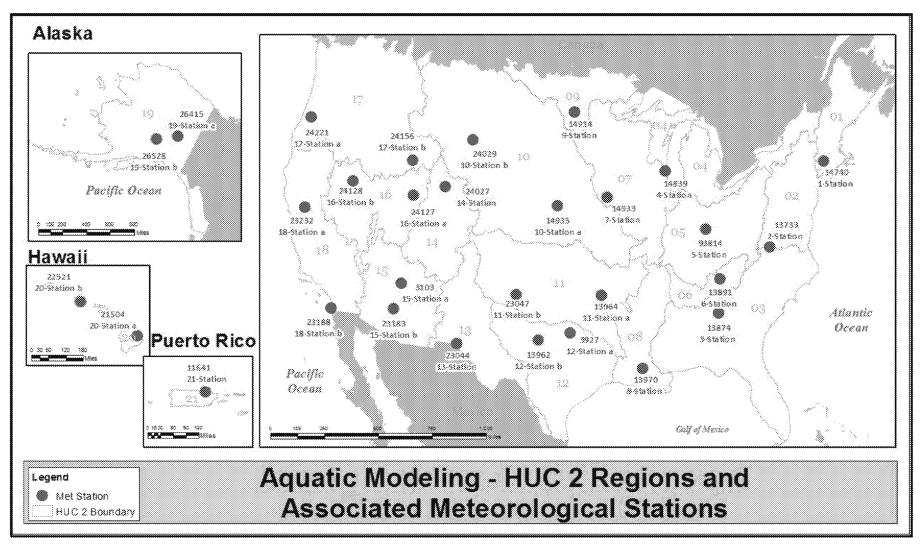


Figure 3-1. Hydrologic Unit Code (HUC) 2-Digit Regions and Associated Metrological Data

3.2 HUC and Use Site Crosswalk

The National Agricultural Statistics Census of Agriculture 2012 (NASS) data along with the Cropland Data Layer (CDL) were used to determine which crops would be modeled within each represented HUC 2. Additionally, specific geographic limitations on how a product may be applied to particular crops were considered when determining what rates would be simulated for different HUC 2 regions. For example, wheat use is only allowed in Idaho, Oregon and Washington. If the NASS data indicated any acreage of a crop was grown in a specific HUC 2, it was assumed that the crop was grown in that HUC 2, and aquatic EECs were generated for these HUC 2 regions for that crop. If there were no reported NASS cropped acres grown within a particular HUC 2, aquatic EECs for that HUC2 region and use pattern were not determined. A crop use layer-HUC 2 Region matrix for methomyl is provided in **APPENDIX 3-1**. Limited NASS data are available for Alaska, Hawaii, and Puerto Rico, and some assumptions on which crops would be simulated in those HUC 2 regions were made.

3.3 Scenario Selection

A PWC scenario was developed for each landcover class and HUC 2 where crops in that landcover were grown based on the NASS 2012 census data. **APPENDIX 3-1** provides a crosswalk between the use site and the landcover used to represent the use site as well as which HUC 2 regions were evaluated for each use pattern. An explanation of how the PWC scenario matrix was developed is provided in **APPENDIX 1-3**.

3.4 Application Practices

3.4.1 Application Method

During application of pesticides, methods of application as well as product formulation used by an applicator can impact the off-site transport of the active ingredient. Label directions (such as spray drift buffers, droplet size restrictions, application equipment and agronomic practices such as soil incorporation) as well as product formulation are considered as part of the development of the use scenario modeled.

There are many different types of methomyl applications included in the master use summary document (APPENDIX 1-2) including those that occur in both agricultural and non-agricultural settings. Application equipment include aircraft, tractors, and irrigation systems. Methomyl applications may occur at different times throughout the year including multiple application to the same crop occurring at different crop stages. When multiple types of applications are allowed on a crop within one calendar year, such as pre-plant or soil incorporation applications along with foliar applications, all applications are simulated considering the appropriate application timing (e.g., dormant, foliar, and post-harvest applications to a crop). Methomyl can be applied as a flowable for all crops as well as granular for corn/sweet corn.

3.4.2 Spray Drift

Methomyl formulations are all sprays except one granular formulation. The spray drift fractions used for all foliar spray in modeling are shown in <u>Table 3-3Table 3-3</u>. Labels for foliar applied products specify that applications must occur at a specified buffer distance of 100 feet for aerial applications and 25 feet for ground applications around natural and artificial bodies of water. Labels for granular products specify that applications must occur at a specified buffer distance (25 feet) to an aquatic area to prevent runoff into the waterbody. No spray drift is simulated for the granular formulation.

Table 3-3. Estimated Spray Drift Fractions for Different Aquatic Bins and Application Methods.

Bin		Spray Dri (unitless)	ft Fraction				
Aquatic	PWC Bin	PWC Bin Generic Number Habitat Dep	Depth (m) ¹	Width (m)¹	100 ft (aerial) and 25ft (ground) buffer		
Bin	Number			, ,	Aerial	Ground	
1	10	Wetland	0.15	64	0.0502	0.0266	
4	4	Reservoir	2.74	82	0.0555 ²	0.03222	
7	7	Pond	2	64	0.0502	0.0266	

¹parameters correspond to the input values used in PWC modeling.

Some methomyl labels specify the use of handheld application equipment (e.g., hose-end sprayers, hand bulb dusters, etc.). Data are not available on the magnitude of spray drift that may result from these types of applications; however, these application methods are not expected to result in substantial drift. Generally, all crops that permit the use of such equipment also permit the use of ground boom or aerial equipment. Such higher-drift (and presumably higher-exposure) application methods were therefore chosen as conservative proxies for all application methods for the relevant crops, for purposes of quantitative exposure estimation.

3.4.3 Application Timing

In selecting application dates for aquatic modeling, EPA considers a number of factors including label directions, timing of pest pressure, meteorological conditions, and pre-harvest restriction intervals. Agronomic information was consulted to determine the timing of crop emergence, pest pressure and seasons for different crops. General sources of information include crop profiles (http://www.ipmcenters.org/cropprofiles/), agricultural extension bulletins, and/or available statespecific use information.

Methomyl may be applied during different seasons, and the directions for use indicate the timing of application, such as, at plant, dormant season, foliar (i.e., when foliage is on the plant), etc. For most methomyl uses, PWC model inputs for the application dates were chosen based on these timings, the crop emergence and harvest timings specified in the PWC scenario, and precipitation data for the associated meteorological station. Application dates were selected to represent conservative and

²Utilizes the drift fraction for the Index Resevoir and 4 m wide stream

EOF concentrations from bin 4 are used as a surrogate for aquatic bins 2 and 5.

Aquatic bin 4 is used as a surrogate for aquatic bin 3.

reasonable estimates. If applicable, dormant seasons were assumed to occur between November and February, the predominant period throughout the country when crops are dormant. Foliar applications were assumed to occur when the crop was on the field in the PWC scenario. When choosing an application date within a time window (*i.e.*, crop emergence or foliar application), the first or 15th of the month with the highest amount of precipitation (for the meteorological station for the PWC scenario) for that time window was chosen. Pesticide loading to surface water is directly affected by precipitation events. Once the first day of application was selected, minimum retreatment intervals were assumed to determine when subsequent applications would occur. If multiple types of applications were allowed on one crop within one year, such as pre-plant or soil incorporation along with a foliar application(s), the retreatment interval was selected to reflect the specified timings. Pre-harvest intervals (the minimum time between an application and harvest) were also considered. Applications would not occur closer to harvest than allowed by the pre-harvest interval. For details on application date selection for use of methomyl, see **APPENDIX 1-3** and **APPENDIX 3-1**.

3.5 Special Agricultural Considerations

3.5.1 Multiple Crop-cycles Per Year

Some labels permit applications on crops that may be planted in rotation (e.g., various vegetables), or that may be grown in multiple crop seasons per year. This phenomenon could result in more methomyl applied to a given field per year, than would necessarily be expected based upon label instructions. While crop rotations are possible for some methomyl uses, rotations were not modeled. As the soil and water metabolism half-lives for methomyl is less than 50 days, accumulation of residues over time is not expected.

3.5.2 PFAM

Methomyl uses do not include rice or cranberries; therefore, modeling using the Pesticide Flooded Application Model (PFAM) was not conducted.

3.5.3 Plant Assessment Tool (PAT)

The Plant Assessment Tool (PAT) is a mechanistic model that incorporates fate (e.g., degradation) and transport (e.g., runoff) data that are typically available for conventional pesticides, to estimate pesticide concentrations in terrestrial, wetland, and aquatic plant habitats. For terrestrial plants, runoff and erosion are modeled using PRZM and spray drift is modeled using AgDRIFT deposition values. The model uses a mixing cell approach to represent water within the active root zone area of soil, and accounts for flow through the terrestrial plant exposure zone (T-PEZ) caused by both treated field runoff and direct precipitation onto the T-PEZ. Pesticide losses from the T-PEZ occur from transport (i.e., washout and infiltration below the active root zone) and degradation. Wetlands are modeled using PRZM/VVWM and are then processed in PAT to estimate aquatic (mass per volume of water) and terrestrial (mass per area) concentrations. Aquatic plants exposure is modeled using the PRZM/VVWM models and the standard farm pond.

3.6 Non-Agricultural Uses and Considerations

As described in the master use summary document (**APPENDIX 1-2**) there is a non-agricultural use site, fly bait application of methomyl around commercial facilities. Given the limited area of use for this use pattern, aquatic modeling was not conducted.

3.7 Aquatic Modeling Input Parameters

The following sections discuss methods used for aquatic modeling. Summaries of the environmental fate model input parameters used in the PWC for the modeling of methomyl is presented in Table 3-4. Input parameters are selected in accordance with the following EPA guidance documents:

- Guidance for Selecting Input Parameters in Modeling the Environmental Fate and Transport of Pesticides, Version 2.1⁵ (USEPA, 2009),
- Guidance for Evaluating and Calculating Degradation Kinetics in Environmental Media^δ (NAFTA, 2012; USEPA, 2012b), and
- Guidance on Modeling Offsite Deposition of Pesticides Via Spray Drift for Ecological and Drinking Water Assessment⁷ (USEPA, 2013)

Table 3-4. Input Values Used for Tier II Surface Water Modeling with PWC.

Parameter (units)	Value (s)	Source	Comments
Organic-carbon Normalized Soil-water Distribution Coefficient (Koc (L/kg-oc))	46	MRID 00161884	Average of four K _{OC} estimates from four soils ranging 36 to 65 L/kg- _{OC} .
Water Column Metabolism Half-life or Aerobic Aquatic Metabolism Half-life (days) and Reference Temperature	6.2 at 20°C	MRID 43325401	Represents the 90 th percent upper confidence bound on the mean of two representative half-life values. Half-life values are representative of aerobic aquatic metabolism ranging from 3.5 to 4.8 days
Benthic Metabolism Half- life or Anaerobic Aquatic Metabolism Half-life (days) and Reference Temperature	39 at 20°C	MRID 4924301	Representative half-life value from one study times three.

⁵ https://www.epa.gov/pesticide-science-and-assessing-pesticide-risks/guidance-selecting-input-parameters-modeling (accessed January 2020)

⁶ https://www.epa.gov/pesticide-science-and-assessing-pesticide-risks/guidance-calculate-representative-half-life-values (accessed January 2020)

⁷The draft guidance is available at www.regulations.gov docket number: EPA-HQ-OPP-2013-0676

Parameter (units)	Value (s)	Source	Comments
Aqueous Photolysis Half- life @ pH 7 (days) and Reference Latitude 40° N latitude, 25°C	50	MRID 43823305	Degradation occurring in photolysis study in natural water
Hydrolysis Half-life (days) ^a	266	MRID 00131249	Chapman and Cole, 1982 at pH 7
Soil Half-life or Aerobic Soil Metabolism Half-life (days) and Reference Temperature	30.4 at 25°C	MRIDs 00008568 43217901 45473401	Represents the 90 th percent upper confidence bound on the mean of five representative half-life values. Half-life values are representative of aerobic soil metabolism ranging from 4.3 to 44 days
MWT or Molecular Weight (g/mol)	162.2 g/mol	MRID 48597001	
Vapor Pressure (Torr) at 30°C	5.4 × 10 ⁻⁶	MRID 41209701	
Solubility in Water @ 25°C, pH not reported (mg/L)	5.5 x 10 ⁴ mg/L	MRID 41402101	
Foliar Half-life (days)	3.0	Willis & McDowell, 1987	90 th %tile mean on 3 methomyl residue foliar persistence half-lives ranging from 1.2 to 2.7 days
Application Efficiency	Aerial: 0.95 Ground: 0.99 Granular: 1.0	Input parameter guidance (USEPA, 2009)	
Drift	Estimated	AgDRIFT	See section 3.4.2

^a The hydrolysis half-life for methomyl was increased from 266 days (used in this assessment) to 522 days, based on hydrolysis data that was reviewed for the 2020 DWA (USEPA, 2020). A sensitivity analysis resulted in less than a 1% change in EECs after increasing the hydrolysis rate to from 266 to 522 days.

3.8 Aquatic Modeling Results

The estimated environmental concentrations (EECs) derived from the PWC modeling based on maximum labeled rates included in the master use summary document, by HUC 2, are summarized for the various aquatic bins in <u>Table 3-5 Table 3-5</u> and

Formatte Formatte <u>Table 3-6</u>Table 3-6, for water column and pore water, respectively. The complete set of modeling inputs and results are available in **APPENDIX 3-1**. PWC runs and post-processed results are provided in **APPENDIX 3-2**. The range of EECs reflects the various application rates and timings for the various crops and scenarios modeled in the HUC 2 regions.

Table 3-5. The Range of PWC Daily Average Water Column EECs for Methomyl.

		Range of 1-in-15 year Daily Average EECs (μg/L)								
HUC 2	Bin 1	Bin 2	Bin 3	Bin 4	Bin 5	Bin 6	Bin7			
HUC 1	738 – 1200	204 - 1300	16.9 - 217	16.9 - 217	204 - 1300	8.51 - 146	8.51 - 146			
HUC 2	652 – 1130	149 - 1769	12.5 - 136	12.5 - 136	149 - 1769	6.73 - 74.0	6.73 - 74.0			
HUC 3	730 – 731	152 - 1715	21.3 - 242	21.3 - 242	152 - 1715	11.0 - 140	11.0 - 140			
HUC 4	554 – 844	140 - 1651	14.7 - 110	14.7 - 110	140 - 1651	7.13 - 68.6	7.13 - 68.6			
HUC 5	975 – 1150	235 - 1727	21.7 - 232	21.7 - 232	235 - 1727	11.6 - 121	11.6 - 121			
HUC 6	609 – 773	119 - 1616	12.4 - 257	12.4 - 257	119 - 1616	6.35 - 147	6.35 - 147			
HUC 7	991 – 1450	214 - 2021	16.7 - 243	16.7 - 243	214 - 2021	8.77 - 136	8.77 - 136			
HUC 8	380 – 501	106 - 958	25.5 - 178	25.5 - 178	106 - 958	13.9 - 100	13.9 - 100			
HUC 9	762 – 1440	98 - 929	11.6 - 106	11.6 - 106	98 - 929	5.85 - 57.5	5.85 - 57.5			
HUC 10a	820 – 1300	190 - 882	22.2 - 188	22.2 - 188	190 - 882	12.8 - 106	12.8 - 106			
HUC 10b	1120 – 1730	266 - 1194	13.5 - 57	13.5 - 57	266 - 1194	7.13 - 31.1	7.13 - 31.1			
HUC 11a	1210 – 1330	319 - 2719	20.2 - 305	20.2 - 305	319 - 2719	10.8 - 150	10.8 - 150			
HUC 11b	1320 – 1640	238 - 2783	24.5 - 162	24.5 - 162	238 - 2783	12.5 – 88.0	12.5 – 88.0			
HUC 12a	1310 – 1550	166 - 2978	16.5 - 298	16.5 - 298	166 - 2978	7.93 - 178	7.93 - 178			
HUC 12b	1520 – 1570	158 - 2455	19.3 - 266	19.3 - 266	158 - 2455	9.30 - 131	9.30 - 131			
HUC 13	1210 – 1430	199 - 2943	10.3 - 244	10.3 - 244	199 - 2943	5.08 - 114	5.08 - 114			
HUC 14	1340 – 1690	229 - 3112	8.17 - 213	8.17 - 213	229 - 3112	4.07 - 109	4.07 - 109			
HUC 15a	1290 – 1700	178 - 4238	8.85 - 259	8.85 - 259	178 - 4238	5.25 - 139	5.25 - 139			
HUC 15b	1620 – 1670	105 - 4369	4.14 - 213	4.14 - 213	105 - 4369	2.42 – 97.0	2.42 – 97.0			
HUC 16a	1300 – 1790	214 - 1945	5.66 - 115	5.66 - 115	214 - 1945	3.02 - 59.6	3.02 - 59.6			
HUC 16b	1090 – 1740	153 - 2181	1.41 - 58.0	1.41 - 58.0	153 - 2181	1.08 - 31.1	1.08 - 31.1			
HUC 17a	638 – 1180	92 - 2105	5.04 - 144	5.04 - 144	92 - 2105	2.71 - 78.4	2.71 - 78.4			
HUC 17b	1130 – 1640	79 - 2022	4.43 - 113	4.43 - 113	79 - 2022	2.67 - 56.3	2.67 - 56.3			
HUC 18a	933 – 1380	236 - 2598	6.14 - 199	6.14 - 199	236 - 2598	3.27 - 117	3.27 - 117			
HUC 18b	865 – 1410	173 - 3065	10.0 - 194	10.0 - 194	173 - 3065	5.09 - 99.7	5.09 - 99.7			
HUC 19a	1320 – 1890	342 - 2129	16.5 - 119	16.5 - 119	342 - 2129	7.87 - 61.1	7.87 - 61.1			
HUC 19b	528 – 596	445 - 2225	16.5 - 140	16.5 - 140	445 - 2225	7.90 - 78.1	7.90 - 78.1			
HUC 20a	435 – 433	162 - 1490	68.1 - 218	68.1 - 218	162 - 1490	48.4 - 219	48.4 - 219			
HUC 20b	661 – 908	130 - 2418	14.1 - 225	14.1 - 225	130 - 2418	11.0 - 145	11.0 - 145			
HUC 21	1020 – 1290	405 - 1907	40.9 - 331	40.9 - 331	405 - 1907	22.1 - 170	22.1 - 170			

Table 3-6. The Range of PWC Pore Water EECs for Methomyl.

uuca	Range of 1-in-15 year Pore Water EECs (µg/L)						
HUC 2	Bin 2	Bin 3	Bin 4	Bin 5	Bin 6	Bin7	
HUC 1	204 - 1406	2.23 - 1098	2.23 - 1098	204 - 1406	1.28 – 188	1.28 – 188	
HUC 2	149 - 1835	1.22 - 283	1.22 - 283	149 - 1835	0.70 - 46.1	0.70 - 46.1	
HUC 3	153 - 1717	2.60 - 157	2.60 - 157	153 - 1717	1.26 - 32.6	1.26 - 32.6	
HUC 4	140 - 1651	1.39 - 78.1	1.39 - 78.1	140 - 1651	0.76 - 14.1	0.76 - 14.1	
HUC 5	238 - 1737	5.22 - 46.0	5.22 - 46.0	238 - 1737	2.84 - 15.2	2.84 - 15.2	
HUC 6	119 - 1617	1.08 - 33.6	1.08 - 33.6	119 - 1617	0.85 - 19.9	0.85 - 19.9	
HUC 7	214 - 2022	2.00 - 226	2.00 - 226	214 - 2022	1.05 - 36.4	1.05 - 36.4	
HUC 8	109 - 959	3.5 - 423	3.5 - 423	109 - 959	2.56 - 66.8	2.56 - 66.8	
HUC 9	98 - 932	1.58 - 37.3	1.58 - 37.3	98 - 932	0.80 - 8.53	0.80 - 8.53	
HUC 10a	191 - 883	2.55 - 28.9	2.55 - 28.9	191 - 883	1.37 - 9.59	1.37 - 9.59	
HUC 10b	269 - 1200	2.48 - 10.9	2.48 - 10.9	269 - 1200	1.37 - 6.62	1.37 - 6.62	
HUC 11a	320 - 2726	1.87 - 70.5	1.87 - 70.5	320 - 2726	0.97 - 27.5	0.97 - 27.5	
HUC 11b	239 - 2786	2.73 - 27.0	2.73 - 27.0	239 - 2786	1.39 - 11.9	1.39 - 11.9	
HUC 12a	166 - 2984	1.96 - 81.8	1.96 - 81.8	166 - 2984	0.91 - 24.4	0.91 - 24.4	
HUC 12b	158 - 2459	1.93 - 60.4	1.93 - 60.4	158 - 2459	0.91 - 15.5	0.91 - 15.5	
HUC 13	199 - 2947	0.87 - 20.5	0.87 - 20.5	199 - 2947	0.43 - 8.41	0.43 - 8.41	
HUC 14	229 - 3118	1.29 - 32.7	1.29 - 32.7	229 - 3118	0.73 - 16.9	0.73 - 16.9	
HUC 15a	178 - 4249	1.44 – 159	1.44 – 159	178 - 4249	0.83 - 51.0	0.83 - 51.0	
HUC 15b	105 - 4374	0.31 - 41.3	0.31 - 41.3	105 - 4374	0.17 - 13.6	0.17 - 13.6	
HUC 16a	215 - 1949	0.87 – 18.0	0.87 – 18.0	215 - 1949	0.48 - 9.80	0.48 - 9.80	
HUC 16b	154 - 2186	0.23 - 8.70	0.23 - 8.70	154 - 2186	0.18 - 5.59	0.18 - 5.59	
HUC 17a	93 - 2115	1.07 - 27.2	1.07 - 27.2	93 - 2115	0.61 - 15.4	0.61 - 15.4	
HUC 17b	79 - 2030	0.92 - 19.6	0.92 - 19.6	79 - 2030	0.55 - 10.8	0.55 - 10.8	
HUC 18a	237 - 2602	1.08 - 45.9	1.08 - 45.9	237 - 2602	0.64 - 26.1	0.64 - 26.1	
HUC 18b	173 - 3068	1.41 - 28.4	1.41 - 28.4	173 - 3068	0.72 - 13.9	0.72 - 13.9	
HUC 19a	344 - 2139	2.95 - 21.7	2.95 - 21.7	344 - 2139	1.49 - 12.1	1.49 - 12.1	
HUC 19b	449 - 2233	3.74 - 24.3	3.74 - 24.3	449 - 2233	1.81 - 15.0	1.81 - 15.0	
HUC 20a	162 - 1490	5.18 – 111	5.18 – 111	162 - 1490	4.65 - 38.8	4.65 - 38.8	
HUC 20b	130 - 2418	1.70 - 22.5	1.70 - 22.5	130 - 2418	1.11 – 15.0	1.11 – 15.0	
HUC 21	405 - 1907	3.26 - 23.5	3.26 - 23.5	405 - 1907	1.78 - 14.8	1.78 - 14.8	

Pore water concentrations for bins 2 and 5 have been estimated using edge-of-field runoff from the dissolved and eroded soil amounts from the ZTS file.

Currently EFED models flowing waterbodies in its FIFRA assessments using the index reservoir, a waterbody with a surface area of 5.26×10^5 m² and a depth of 2.74 m, with a watershed area of 1.728×10^6 m². This conceptual model is based upon the Shipman Reservoir in Illinois and has been reviewed by EPA's FIFRA SAP. Although the dimensions are smaller than those of a bin 3 or 4 and the flowrate is much lower, EFED has confidence in the estimated concentrations developed using the index reservoir and believes these EECs can be used as a conservative surrogate for bins 3 and 4 until EFED can validate a conceptual model for bins 3 and 4.

3.9 Available Monitoring Data

Monitoring data discussed in this section are considered in the downstream analysis and the weight of evidence analysis in the MAGtool (discussed in **Chapter 4**).

3.9.1 Field Studies

Field scale monitoring studies, where the applications were known and residues in water following applications were followed, were requested in the Methomyl Registration Standard issued in 1987, to support the reregistration of methomyl. The aquatic residue monitoring studies for various use patterns were conducted in different states: sweet corn in Illinois and Georgia; apples in Michigan; lettuce in Florida; and cantaloupe in California. These studies are briefly summarized in the following sections. Methomyl was found in aquatic environments adjacent to treated fields in all five studies at maximum concentrations ranging from 1.7 up 175 μ g/L. Runoff water leaving treated fields had concentrations as high as 1,320 μ g/L.

3.9.1.1 Illinois Sweet Corn Study (MRID 43708802)

In Illinois, two sites planted to sweet corn were treated with 16 daily aerial applications of 0.45 lbs a.i./A, for a total of 7.2 lb a.i./A. A foliar dislodgeable residue study indicated that the methomyl easily removable from foliar surfaces decreases rapidly, with 75-78% of the applied dissipating within 7.5 hours after application. Methomyl dissipated in the soil with a half-life of 6.5 days. Samples were collected from two canals and one pond adjacent to the treated fields. The maximum concentrations measured in canal water at the two sites were $5.0-26.5~\mu g/L$. The maximum 96-hour and 21-day peak concentrations at the canal sites ranged from 1.5 to 10 $\mu g/L$ and from 0.8 to 5.8 $\mu g/L$, respectively. The median methomyl concentration in the pond was 0.8 $\mu g/L$; the maximum concentration was 2.0 $\mu g/L$.

3.9.1.2 Georgia Sweet Corn Study (MRID 43744401)

A Georgia site planted to sweet corn included flumes, diversion walls, and ditches constructed to direct field runoff directly into a pond. The site was treated with 29 aerial applications of 0.3-0.5 lbs a.i./A, at 1 day intervals, for a total of 11.25 lbs a.i./A. The average half-life of methomyl in soil was 9 days. Pond concentrations peaked 19 days after the first application and were at or near the limit of quantification 16 days after the final application. Samples were collected from two stream stations as well as the pond. Methomyl concentrations in water samples collected from an adjacent stream ranged from 1.1 to 175 μ g/L. Median methomyl concentrations during the application period were 5.5, 3.4 and 0.95 μ g/L, respectively for the upstream, pond, and downstream stations, respectively. The 96-hour and 21-day average concentrations were 6.7 and 4.2 μ g/L, respectively.

3.9.1.3 Michigan Apple Orchard Study (MRID 43708801)

Two sites were studied in Michigan. At one site, apple orchards surrounded a pond on three sides. At the other site, apple orchards surrounded a pond on all sides. Each orchard received five applications of methomyl at a rate of 1.35 lbs a.i./A, for a total of 6.75 lbs a.i./A at 5-day intervals with an air blast sprayer. Median methomyl concentrations in soil ranged from 0.932 to 12.500 mg/kg. The half-life of methomyl in soil was 26 days during a dry period, decreasing to 8 days after rainfall events. The half-life of methomyl residues on apple foliage was 4 days. Only 19% to 50% of the total methomyl applied actually reached spray drift cards on-site. The most noticeable increase in methomyl concentration in pond water was associated with the application day which had the highest wind speeds. Deposition cards placed on the surface of the pond showed that the pond received from 0.2% to 0.44% of the application rate. Methomyl concentrations in runoff water ranged from 300 to 1320 μ g/L during the application period and <20 μ g/L 2-3 weeks later. Median methomyl concentrations in the pond water ranged from 0.16 to 13.3 μ g/L during the application period. Concentrations dropped below the quantification limit of 0.2 μ g/L within 9 to 30 days after the final application. The registrant concluded that spray drift was the primary source of methomyl in the pond. PRZM/EXAMS simulations run on the same sites served as good predictors of the environmental fate of methomyl.

3.9.1.4 Florida Lettuce Study (MRID 43708804)

Two fields planted to lettuce in Florida in the Lake Apopka area were treated with ten aerial applications of 0.9 lbs a.i./A at 2-day intervals for a total of 9.0 lbs a.i./A. Methomyl dissipated rapidly from the surface layer with a half-life of between 4 and 5 days and slower from deeper soil layers with half-lives between 8 and 10 days. Median methomyl concentrations were 16 and 47 ppb in the lateral canals; 3 and 6 ppb in the main canals. The peak 96-hour and 21-day average concentrations reaching Lake Apopka were 0.8 and 0.3 μ g/L, respectively. The highest measured concentration entering the lake was 1.7 μ g/L measured immediately after the canals draining the fields were pumped down in expectation of a rain storm; concentrations fell below the limit of quantification within six days. Concentrations in the lake were generally two orders of magnitude less than those of the canals.

3.9.1.5 California Cantaloupe Study (MRIDs 43708803 and 43823304)

Two cantaloupe fields in Fresno were treated with six aerial applications of methomyl at 0.90 lbs a.i./A each. One field was irrigated five times and the other four times. The half-life of methomyl in the soil was between 12 and 21 days in the period after the last application. The mean methomyl concentration measured in the surface waters receiving irrigation runoff was 0.86 to 4.6 μ g/L. Maximum concentrations leaving the two sites were 71 and 96 μ g/L. The total amount leaving the field as runoff was less than 0.2% of the amount applied.

3.9.2 General Monitoring Data

Examination of the EPA 303(d) list of impaired waters⁸ indicates no impairments caused by methomyl, as of December, 2019.

Water monitoring data were obtained from the National Water Quality Monitoring Council's Water Quality Data Portal (USEPA and USGS, 2021) in 2019, which is supplied by the USGS NWIS and EPA

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⁸ https://iaspub.epa.gov/waters10/attains_nation_cy.control?p_report_type=T

STORET databases of monitoring data collected across the United States by numerous federal, state, tribal and local agencies. Prominent contributors to this database include the USGS National Water-Quality Assessment Program (NAWQA) and various state and local agencies. Data were also specifically obtained from the USEPA/USGS Pilot Reservoir Monitoring Program, USDA Pesticide Data Program (PDP; focused on raw water samples), California Department of Pesticide Regulation (CDPR), and the Washington State Department of Ecology and Agriculture (WSDE/WSDA). Some of the data may occur in more than one database.

In general, the surface water monitoring data include sampling sites that represent a range of aquatic environments including small and large water bodies, rivers, reservoirs, and urban and agricultural locations, but are limited for some areas of the United States where methomyl use occurs. Also, the sampling sites, as well as the number of samples, vary by year. The vulnerability of the sampling site to methomyl contamination varies substantially due to use, soil characteristics, weather and agronomic practices. None of the monitoring programs examined to date were specifically designed to target methomyl use. Therefore, peak concentrations of methomyl likely went undetected in these programs. The various monitoring programs did not detect methomyl with high frequency, but methomyl detections ranged from <0.01 μ g/L up to 400 μ g/L (groundwater sample from 1987). Many of the high detections were historical and were reported in the late 1980s, but several more recent detections exceeded 10 μ g/L (up to 55 μ g/L in Monterey County, CA; Chualar Creek, 2010). The extent to which historical values represent current agronomic or labeled use instructions is uncertain.

Therefore, while there are many individual samples collected and analyzed for methomyl across the United States, it would not be appropriate to combine these data sources to generate exposure estimates or to use these datasets to represent exposure on a national or even regional basis. While these data demonstrate potential exposure, using the measured concentrations as an upper bound exposure estimate would not be a reasonable approach for the reasons given above, including limited sample frequency, limited use information, and sampling site variability, on a national or even a regional basis. Therefore, model estimated concentrations should be considered a suitable upper bound concentration for methomyl.

3.9.2.1 Water Quality Portal

Surface water and groundwater methomyl data were obtained in 2019 in a download of data from the Water Quality Data Portal (http://www.waterqualitydata.us/).

A significant portion of the data obtained from the water quality portal has been supplied through NAWQA, a national-scale ambient water quality monitoring program that contains monitoring data for pesticides in streams. The database includes an extensive amount of data for methomyl; however, the NAWQA monitoring program was not designed to specifically target methomyl use. Specifically, the sample timing and frequency were not designed to correspond with methomyl applications. The monitoring sites were not selected based on known methomyl treatment areas, although there are some sampling locations in high methomyl use areas. In general, sample frequencies are sporadic and range from once per year to a couple times per month depending on the site and year. For these reasons, the data included in the NAWQA dataset are expected to underestimate peak methomyl concentrations. The magnitude of this underestimation is unknown.

The Water Quality Portal surface water monitoring data for methomyl are highlighted in Error! Reference source not found. Table 3-7, which provides a summary of the results by HUC 2 region, with sampling occurring from 1982 to 2019 at over 4,310 sites with a maximum detected concentration of 12 µg/L.

Table 3-7. Water Quality Portal Monitoring Data Summarized by 2-digit HUC.

HUC-2¹	Years	Number of Sites	Number of Samples	Number of Detections	Measured Detection Range (μg/L)
01	1993 - 2019	102	597	1	0.00316
02	1988 - 2019	414	2400	7	0.00312 - 0.19
03	1982 - 2019	451	4056	23	0.00084 - 1.9
04	1982 - 2019	226	1156	3	0.00327 - 0.00843
05	1989 - 2019	81	1236	7	0.00315 - 0.0829
06	1988 - 2016	68	399	1	0.406
07	1990 - 2019	146	1886	2	0.00518 - 0.86
08	1986 - 2019	103	1182	18	0.00302 - 0.65
09	1992 - 2019	130	351	0	nd
10	1983 - 2019	279	2283	26	0.00203 - 0.107
11	1986 - 2019	116	741	1	0.00146
12	1982 - 2018	252	1983	10	0.044 – 3
13	1986 - 2018	77	359	1	0.00107
14	1988 - 2019	142	534	11	0.00153 - 0.0411
15	1991 - 2018	90	589	6	0.00076 - 0.43
16	1977 - 2019	156	540	0	nd
17	1988 - 2019	855	8375	121	0.00141 - 1.33
18	1982 - 2019	592	2226	119	0.00155 - 12
19	1998 - 2015	2	14	0	nd
20	1999 - 2017	26	46	2	0.0174 - 0.0275
21	2013 - 2013	2	2	0	nd

nd – not detected.

Reported concentrations in groundwater were as high as 400 μ g/L. That maximum value was reported in New Jersey in 1987. Other reported values that exceed 1 μ g/L (N=7) were reported from NY, NJ, and MO with values ranging from 1 to 8.1 μ g/L. An additional 12 groundwater detections were reported at levels between 0.005 μ g/L and 0.94 μ g/L. The detection frequencies in groundwater and surface water samples in the database were 0.1% and 0.6%, respectively. The range of limit of detections (LODs) for methomyl is 0.004 μ g/L to 80 μ g/L.

From January 2016 to January 2018, water quality data were available from the USGS National Water Information System (NWIS), the EPA STOrage and RETrieval (STORET) Data Warehouse, and the USDA ARS Sustaining The Earth's Watersheds - Agricultural Research Database System (STEWARDS). For methomyl, there were a total of 5097 samples with 58 samples show detection greater than 0.0007 μ g/L. Among these samples, 9 detections are greater than 0.1 μ g/L. The top two samples show greater

than 0.3 μ g/L (0.356 and 0.336) both are detected by the State of Oregon Department of Environmental Quality.

3.9.2.2 USDA Pesticide Data Program

The USDA Pesticide Data Program (PDP) Water Monitoring Survey is designed to collect monitoring data on pesticide residues in drinking water. This is an ambient water monitoring program. For the purposes of this assessment only raw water samples are considered. PDP began testing for pesticide residues in drinking water sources in 2001. Samples have been collected from 82 locations in 28 states and the District of Columbia; however, only a subset of these sampling locations were sampled each year. While methomyl was monitored as part of the PDP, the program was not designed to specifically target methomyl —the sample timing and frequency were not designed to correspond with methomyl applications. Although there are some sampling locations in methomyl use areas, the monitoring sites were not selected based on known methomyl use areas. For these reasons, the data included in the PDP program are expected to underestimate methomyl concentrations. The magnitude of this underestimation is unknown. There was one detection of methomyl reported in the PDP data in raw intake water as summarized in Table 3-8Table 3-8.

Table 3-8. USDA Pesticide Data Program Monitoring data for Methomyl.

	/	
Parameter	Methomyl	
Source	Raw Intake Water	
Sampling Years	2010 to 2015	
Number of Samples	697	
Sample Frequency	bimonthly	
Qualified Detections	1	
Frequency of Detections	<0.1%	
Maximum Detection	12.2 ng/L (2010)	
LOD	LOD 7.5 ng/L	

3.9.2.3 California Department of Pesticide Regulation

The California Department of Pesticide Regulation (CDPR) maintains a surface water database of pesticide detections in surface waters (large and small water bodies) for the entire state. This is an ambient water monitoring program. In general, sample frequencies are sporadic and range from once per year to twice per month depending on the site and year. The sampling frequency and timing represented in the dataset do not specifically target methomyl applications; however, there are some sampling sites located within areas known to have high methomyl use. Because the sampling was not designed to monitor for methomyl, it is expected that the CDPR data underestimate methomyl concentrations. The magnitude of this underestimation is unknown.

The maximum detection was 55 μ g/L in 2010 from a sample taken from Chualar Creek (a tributary of the Salinas River). Overall, 67 samples had concentrations greater than 1 μ g/L ranging from 1991 to 2015. There are 28 samples greater than 1 μ g/L were collected post 2010, with most of the highest detections occurring in Monterey and Stanislaus counties. The samples with the highest concentrations typically

occur in the spring and summer. CDPR data for methomyl in surface water are highlighted in <u>Table 3-9</u>.

Table 3-9. CDPR Surface Water Monitoring Data for Methomyl.

Parameter	Methomyl		
Sampling Years	1991-2015		
Number of Samples	5136		
Sample Frequency	Varied		
Qualified Detections	464		
Frequency of Detections	9%		
	55.3 μg/L		
Maximum Detection	2010		
	Monterey County, CA		
	Chualar Creek (ID # 371481)		
LOQ	0.001 to 10 μg/L		

Monitoring data from 2015 to 2017 were also examined using the California Department of Pesticide Regulation's Surface Water Database (SURF)9. The report period was from 01/01/2016 to 04/20/2017. There were a total of 311 samples with 88 samples with concentrations greater than 1 μ g/L. Among these samples, 81 samples had a concentration of 2 μ g/L, with a LOQ of 1 μ g/L. The seven remaining samples were all collected in Monterey County, four of which had concentrations greater than 2 μ g/L (4.94, 4.28, 3.55 and 2.12 μ g/L).

3.9.2.4 STORET Data Warehouse

STORET Data Warehouse is a repository for water quality, biological, and physical data and is used by state environmental agencies, EPA and other federal agencies, universities, private citizens, and many others. The sampling frequencies vary by the source of the submitted data and samples collected are not targeted to methomyl uses, nor does the database contain use information.

EPA evaluated the data in the STORET database for 1986 to 2015, while data after 2015 was assessed from the Water Qualtiy Portal. The maximum detection reported in STORET (Table 3-10Table 3-10) is 50 μg/L (two detections), which have been reported by EPA's Region 10 (historical data) from 1987 and by Arizona Department of Environmental Quality in 1994. There were a number of additional detections in groundwater that ranged from 4 μg/L to 20 μg/L that were mostly from the late 1980's. However, one detection reported by the Arizona Department of Environmental Quality and one detection reported by the California State Water Resources Control Board reported methomyl concentrations of 12 μg/L in 2001 and 2006.

Table 3-10. STORET DATA Warehouse Monitoring Data for Methomyl.

Parameter	Methomyl
Sampling Years	1986-2015
Number of Samples	5400
Sample Frequency	Varied
Qualified Detections	190

⁹ SURF database: http://cdpr.ca.gov/docs/emon/surfwtr/surfcont.htm

Formatte

Parameter	Methomyl
Frequency of Detections	3.5%
Maximum Detection	50 μg/L 1987
	New Jersey; Arizona Groundwater
LOD	Varied

3.9.2.5 Washington State

Sampling focused on salmon-bearing streams in five different basins within Washington (Sargeant, et al, 2010; Sargeant, et al, 2013). Primarily weekly sampling was conducted during the pesticide use season; however, some daily sampling was also conducted. While the study did not specifically target methomyl use, nor did the report provide pesticide use information, some pesticide use survey data was obtained from WSDA.

There were five detections of methomyl that were estimated at $0.004 \,\mu\text{g/L}$ to $0.012 \,\mu\text{g/L}$, mostly in the Lower Yakima Agricultural Watershed. Use of methomyl during the year of the study included alfalfa seed, onion, apple, blueberry, and potato. Methomyl detection frequency was approximately 1%.

3.9.2.6 Washington State Department of Agriculture

The Washington State Department of Agriculture provided monitoring data on methomyl during the comment period of the draft Biological Evaluation. More than 5,000 surface water samples were collected from 36 distinct sites in Washington State. The limit of quantitation was 10 ng/L for most samples. There were 78 samples detections with a maximum concentration of 40 μ g/L. These data will be utilized in the MAGtool analysis and downstream monitoring analysis.

3.9.2.7 Open Literature

Battaglin *et al.* (2009) investigated the occurrence of a number of pesticides and their degradates in vernal pools in Washington DC, Maryland, Iowa, and Wyoming. Site locations were chosen based on correlation with glyphosate use patterns (areas where glyphosate was used in agriculture or invasive plant control. Methomyl was an analyte in this study, but was not detected at the reporting limit of 0.02 μ g/L. The study appeared to collect single samples from each site, and site locations were not designed to correlate with methomyl use.

3.9.2.8 Atmospheric

Air monitoring data collected from the 1960s through the 1980s, and summarized by Majewski and Capel (1995), do not indicate the presence of methomyl in the atmosphere, due in large part to the lack of testing for methomyl. The authors' review a single study which tested for methomyl in ambient air at three residential sites near an agricultural area in Salinas, California which were sampled during a high pesticide use month. Methomyl was not detected at any of the air monitoring sites (the level of detection was 35 nanograms per cubic meter).

The January 2008 report by the Western Contaminants Assessment Project (WACAP) yielded no detects of methomyl in the atmosphere or evidence of long range transport. A copy of the report can be found at https://www.nature.nps.gov/air/Studies/air_toxics/WACAPreport.cfm. A report generated by Daly et

al. and published by the American Chemical Society in 2007 titled Pesticides in Western Canada Mountain Air and Soil¹⁰ did not sample for methomyl which is expected since long range transport and volatilization of methomyl are not expected to be major pathways of concern.

3.10 Aquatic Exposure Summary

Model-derived EECs represent an upper bound on potential exposure as a result of the use of methomyl. Comparing the concentrations in the medium and high flowing and static bins (3, 4, 6, and 7) to the highest measured concentrations, the modeled values are roughly the same order of magnitude or an order of magnitude greater than the measured concentrations. The medium and high flowing and static bins were used for comparison purposes as these would seem to represent typical waterbodies considered for ambient water monitoring, as they typically have flow and water present all year. As recommended by the NRC in the 2013 NAS report, general monitoring data are not recommended to be used to estimate pesticide concentrations after a pesticide application or to evaluate the performance of EPA's fate and transport models. However, EPA believes monitoring data can be used as part of the weight-of-evidence evaluation to evaluate potential exposure.

3.11 Uncertainties in Aquatic Modeling and Monitoring Estimates

Exposure to aquatic organisms from pesticide applications is estimated using PWC EECs. Regional differences in exposure are assessed using regionally-specific PWC scenarios (*e.g.*, information on crop growth and soil conditions) and meteorological conditions at the HUC 2 level (**Section 3.3. Scenario Selection**). The information used in these scenarios is designed to reflect conditions conducive to runoff. In instances where PWC scenarios do not exist in a HUC 2, surrogate scenarios from other HUCs are used. For fields where agricultural practices that result in less conservative scenario parameters are employed (*i.e.*, conditions less conducive to runoff and pesticide loading of waterbodies), the potential for lower EECs would be expected.

The static waterbodies modeled with PWC are fixed volume systems with no outlet, resulting in the potential for accumulation of pesticide over time. Effects due to the increase and/or decrease of the water level in the waterbody and thus the concentration of pesticide in the waterbody are not modeled.

Flowing waterbodies are modeled in the PWC using the constant volume and flow through custom waterbody option. Effects due to the increase and/or decrease of the water level and flowrate in the waterbody and thus the concentration of pesticide in the waterbody are not modeled.

The assessment relies on maximum use patterns (**APPENDIX 1-2**). In situations where use patterns are less than the labeled maximums, environmental exposures will be lower.

The aquatic modeling conservatively assumes that the waterbody abuts the treated area. As such, any reduction in loading from runoff that could occur as the result of managed vegetative filter strips or unmanaged naturally-occurring interfaces between treated areas and waterbodies are not taken into account.

¹⁰ Gillian L. Daly, Ying D. Lei, Camilla Teixeira, Derek C. G. Muir, and Frank Wania. 2007. Pesticides in Western Canada Mountain Air and Soil. Environmental Science & Technology 2007 41 (17), 6020-6025. DOI: 10.1021/es0708480

The aquatic modeling assumes a constant wind of 10 mph blowing directly toward the waterbody (Section 3.4.2. Spray Drift). These assumptions are conducive to drift transport and result in maximum potential loading to the waterbody. However, in many situations the wind will not be blowing constantly and directly toward the water body at this speed; therefore, aquatic deposition will likely be less than predicted. Additionally, many labels and applicator best management practices encourage not applying pesticides when the wind is blowing in the direction of sensitive areas (*i.e.*, listed species habitat). Lastly, reductions in spray drift deposition due to air turbulence, interception of spray drift on nearby plant canopy, and applications during low wind speeds are not taken into account in the spray drift estimates; therefore, loading due to spray drift may be over-estimated.

There is uncertainty associated with the selection of PWC input parameters. In this regard, one of the important parameters that can impact concentration estimates is the selection of application dates (Section 3.4.3. Application Timing); runoff and potential pesticide loading are greatest when applications immediately precede major precipitation events. Although the pesticide application dates are selected to be appropriate and protective (*i.e.*, selected with consideration for label restrictions and simulated cropping dates, pest pressures, and high precipitation meteorological conditions), uncertainty nevertheless results because the application window (the time span during a season that a pesticide may likely be applied) for a pesticide may be wide and actual application dates may vary over the landscape. While data sources exist that allow for determination of historical application dates (*e.g.*, California's Pesticide Use Report and pesticide use surveys), it is uncertain how these dates reflect future application events. Additionally, the PWC model uses the same application dates for the 30-year simulation. While it is unlikely that an application would occur on the same dates every year for 30 years, this modeling process allows for a distribution of EECs to be developed that captures the peak loading events.

The PWC is a field-scale model. Flowing water bodies such as streams and rivers with physical parameters consistent with aquatic bins 3 and 4 have watershed areas well beyond those of typical agricultural fields. Initial modeling efforts in previous BEs, applying the field-scale model to these large watersheds and using the same scenario parameters as those used for the other bins, resulted in extremely high EECs which have not been observed in the environment, nor would be expected to occur due to fluid dynamic processes such as advective dispersion (Figure 3-2Figure 3-2), where the peak concentration is dampened as it moves from a low flowing stream (bin 2) to a higher flowing river (bins 3 and 4). It is acknowledged that a watershed/basin-scale model capable of evaluating the impact of pesticide and water transport at the field-scale and aggregating these loadings to waterbodies at the larger watershed-scale is needed to evaluate these flowing aquatic systems.

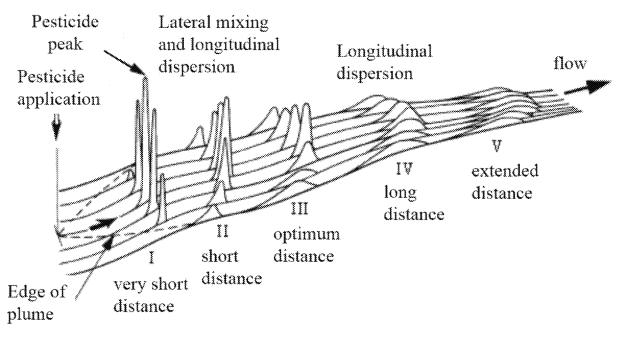


Figure 3-2. Effect of Pesticide Concentration via Advective Dispersion

3.12 Uncertainties the Plant Assessment Tool (PAT)

The PAT model does not account for site specific field management and hydrology (e.g., terracing, contour farming, runoff and erosion controls, irrigation/drainage ditches, rills and creeks) which may result in less opportunity for runoff into the T-PEZ. Many different factors (e.g., slope; surface roughness; flow path length; etc.) can influence the occurrence, distance of, and prevalence of runoff onto the T-PEZ. These factors may vary greatly between different application sites (e.g., corn; wheat; potato; grape; bare field; turf).

The PAT model assumes that the water leaving the field as surface runoff is driven primarily by the amount of rainfall and the curve number, which is a function of the land use (*i.e.*, row crops, pasture, fallow), management (*i.e.*, straight row cropping, conservation tillage, etc.), and hydrologic soil conditions (*i.e.*, high runoff potential with very slow infiltration rates; Young and Fry, 2016). Runoff leaving the field is assumed to enter the T-PEZ along the downslope field edge and coverage of the T-PEZ area conceptually happens instantaneously as the calculations are on a daily timestep rather than shorter timestep (*e.g.*, hourly). As a result, the T-PEZ does not account for differences in the runoff loading (*e.g.*, point entry and fan shaped sheet flow vs. uniform sheet flow entry), gradients in concentration due to interception and infiltration (*e.g.*, buffering capacity of the T-PEZ), rain intensity and infiltration capacity relationships (*e.g.*, pulsed rain events vs. one intense rain event). These natural features of the landscape may result in higher concentrations from runoff at the edge of the T-PEZ nearer the treated field than estimated in the model.

There are many different types of wetlands (e.g., depressional, groundwater fed, flow through, permanently flooded, and ephemeral) that may be present in landscapes receiving runoff from pesticide use sites. The default WPEZ model was selected to be representative and conservative (in terms of final pesticide concentrations) and acts as a surrogate for other types of wetlands. This assumption may result in overestimation of pesticide loading and fate than would be observed in some wetland systems.

4 Measures of Terrestrial Exposure

Terrestrial animals may be exposed to methomyl through multiple routes of exposure, including diet, drinking water, dermal and inhalation exposure. Terrestrial dietary items may consist of plants, invertebrates or vertebrates (amphibians, reptiles, birds or mammals) that inhabit terrestrial areas or aquatic dietary items (fish, invertebrates or plants). However, due to methomyl's low log k_{OW} value (0.12), significant bioaccumulation in aquatic food items is not expected and potential risk from this route of exposure is considered low. Therefore, estimates of exposure through consumption of aquatic food items using KABAM or BCF values are not calculated. A detailed discussion of the conceptual framework for estimating terrestrial exposure concentrations is provided in **ATTACHMENT 1-1**.

Two major parameters are used in terrestrial exposure modeling to characterize a species: body weight and diet. Estimates of body weights are necessary to estimate dose-based exposures through diet, drinking water, inhalation and dermal exposure routes. Information on the dietary requirements of listed species are necessary to determine relevant exposures through consumption of contaminated prey. Species-specific assumptions related to diet and body weight are provided within the model. The foliar dissipation half-life of the chemical can also impact the duration of exposure to predicted terrestrial EECs. A foliar dissipation half-life of 3 days is used for methomyl, based on data reported by Willis and McDowell (1987).

To improve efficiency and expand EFED's modeling capabilities to other, non-dietary routes of exposure for terrestrial organisms, models have been developed to integrate the relevant exposure pathways and allow for batch processing of multiple analyses. For use in the pilot BEs (USEPA, 2016d), the Terrestrial Effects Determination (TED) tool was developed, which integrated T-REX, T-HERPS, the earthworm fugacity model, components of KABAM and AgDRIFT into one model platform. As part of the development of the draft biological opinion for chlorpyrifos, diazinon and malathion, the TED tool was converted to the terrestrial MAGtool, which further expanded the TED tool to predict the magnitude of effect at a population scale and incorporate the degree of overlap of a species range with potential use sites for a chemical (and associated off site transport areas) into the effects determination. The MAGtool has replaced the TED tool for modeling terrestrial exposure in the biological evaluations. Additional technical information on the MAGtool, can be found in the Revised Methods and the model documentation. ¹¹

When the MAGtool is run for each species, terrestrial exposure concentrations are uniquely calculated for each species depending on relevant use overlap with the species range, available usage data, application rates associated with these relevant uses and the dietary items, habitat and obligate

¹¹ Available online at: https://www.epa.gov/endangered-species/models-and-tools-endangered-species-pesticide-assessments

relationships for that species. As EECs will vary for each species, they are determined for each species in the individual effects determinations(**APPENDIX 4-1**).

To provide a bounding of potential terrestrial EECs used in the effects determinations, EECS were calculated for the range of application rates for methomyl (a minimum application rate of 0.45 lb a.i./A with 1 application per year and a maximum application rate of 0.9 lb a.i./A with 24 applications per year) and are provided below in **Table 3-12**. How the EECs will be applied will vary with each step of the analysis (e.g., use of upper bound EECs in Step 1 vs. distribution of EECs in Step 2) and could be slightly higher with mid-range application rates applied multiple times. Additionally, other information considered in Step 2 (e.g., typical use rates, use rates based on maximum usage in a species range, distribution of EECs, etc.), could alter the EECs used to assess a species exposure. All uses for methomyl and associated application rates are provided in **APPENDIX 1-2**. <u>Table 3-11 Table 3-12</u> summarizes the mean and upper bound dietary-based EECs and the associated base model that is used in the MAGtool to predict the EECs. Methomyl uses also include granular and fly bait formulations; these are analyzed separately and are discussed in **APPENDIX 4-5**.

Table 3-1112. Mean and Upper Bound Dietary Based EECs Calculated for Food Items Consumed by Listed Mammals, Birds, Terrestrial-phase Amphibians or Reptiles Based on Foliar Applications. Values represent potential exposures for animals feeding on the treated field or in adjacent habitat directly adjacent to the field.

Food Item	Model	Minimum application rate (0.45 lb a.i./A x 1 application/year)		Maximum application rate (0.9 lb a.i./A x 24 applications/year)	
		Upper Bound	Mean	Upper Bound	Mean
Short Grass	T-REX	108	38	584	207
Tall Grass, nectar and pollen	T-REX	50	16	268	88
Broadleaf plants	T-REX	61	20	328	109
Seeds, fruit and pods	T-REX	7	3	36	17
Arthropods (above ground)	T-REX	42	29	229	158
Soil-dwelling invertebrates (earthworms)	Earthworm fugacity	0.02	NA¹	0.49	NA ¹
Small mammals (15 g, short grass diet)	T-HERPS	103	36	1031	365
Large mammals (1000 g, short grass diet) ²	T-HERPS	17	6	165	58
Small birds (20 g, insect diet)	T-HERPS	48	33	2535	1753
Small terrestrial phase amphibians or reptiles (2 g; insect diet)	T-HERPS	2	2	124	85

Fish, aquatic	NA ³	
invertebrates and		
aquatic plants		

¹NA as upper bound and mean residues only applicable to items dependent on residues on foliage

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² Also represent residues in carrion.

³ NA due to lack of bioaccumulation of methomyl in aquatic dietary items

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